We would like to study the tunneling of an electron out of a localized state that is coupled to a large potentially infinite system. For example a quantum dot with an electron that can tunnel into a large graphene sheet or nanotube.

Let us call the localized object A. We have some method of knowing the initial state of the electron which is localized in A --- for example we have a tight binding Hamiltonian description so we can isolate the Hamiltonian for A only and find a localized eigenstate of interest.

We will call the localized starting state in A $\phi_A(r)$

We call the eigenstates and eigenvalues of the total system of A plus the large sheet or nanotube $\psi_n(r)$ and E_n

The wave function of the electron at any given time is $\Psi(r,t)$

We want to solve for the time dependent wave function given initial state $\Psi(r,t)=\phi_A(r)$

Solution is easy: ($\hbar=1$)

$$\Psi(r,t)=\sum_n \psi_n(r)\langle\psi_n|\Psi(t=0)\rangle e^{-iE_nt}$$

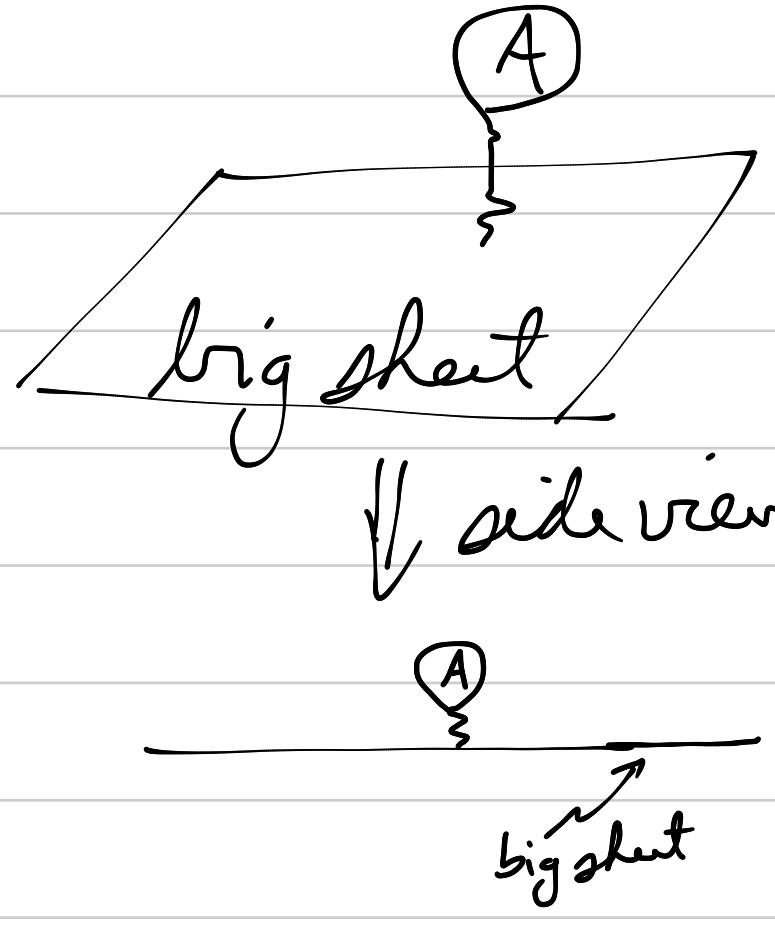
$$=\sum_n \psi_n(r)\langle\psi_n|\phi_A\rangle e^{-iE_nt}$$

What is "amount" left in A?

$$\langle\phi_A|\Psi(r,t)\rangle=\sum_n|\langle\phi_A|\psi_n\rangle|^2 e^{-iE_nt}$$

and prob. of staying in A is $P_A(t)=|\langle\phi_A|\Psi(r,t)|^2$

(We can sum over various states in A if needed).

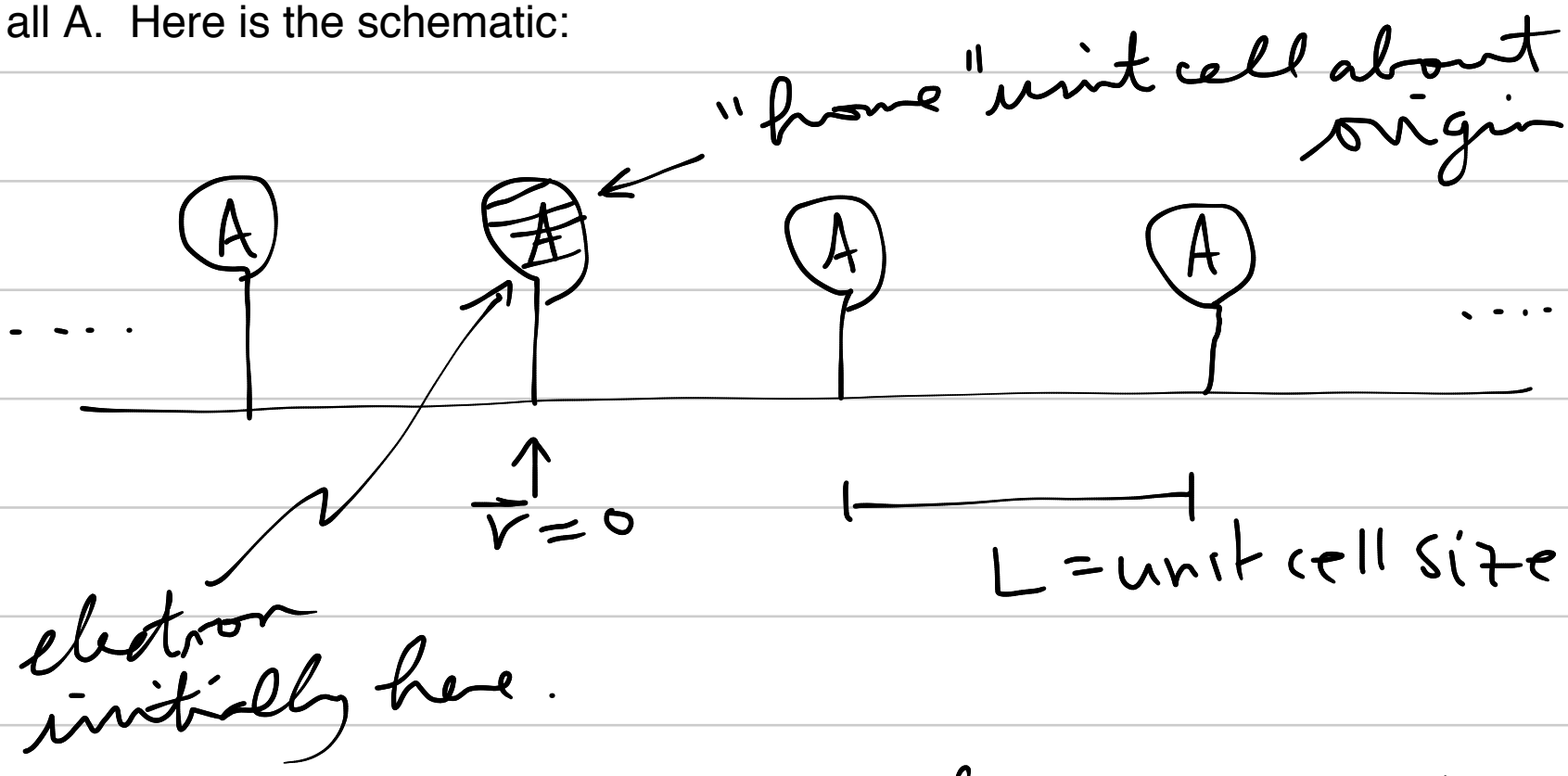


This is formally correct but not very practical for computation since we can never model an infinite sheet. Some obvious approaches:

1. Make the sheet finite and very big and try to converge versus its size. In principle guaranteed to work, in practice can be very slow to converge.
2. Take a finite sheet and glue it along the edges to a mathematically infinite sheet by using the infinite ideal sheet Green's function or similar approach. As long as the finite sheet is big enough to be unaffected by A at the edges, this will take one immediately to the infinite limit. Also one knows the solution of an infinite ideal sheet since one can solve it separately using Bloch's theorem. The main difficulty comes in the complexity of doing the gluing.
3. Take a finite sheet and A and make it structurally periodic by making infinite copies of it. Then one has again a periodic system with a finite sized unit cell and one can use Bloch's theorem to get the eigenstates and thus be in the infinite size limit easily. This is easiest to implement but one is not solving the problem posed. One is solving an electron leaving A not into an infinite sheet but into an infinite sheet with periodic copies of A on it. Whether this creates some serious error or not that converges poorly with unit cell size is unclear at this point.

Let us then choose option 3 and see what it means.

Please note that our starting state is the electron on A in a specific unit cell and not delocalized over all A. Here is the schematic:



so $\Psi(r,0) = \phi_A(r)$ is localized on one A around $r=0$.

Eigenstates of periodic system are Bloch states : $\psi_{nk}(r)$ & E_{nk}

Repeating time evolution:
just put k in sum!

$$P_A(t) = |\langle \phi_A | \Psi(t) \rangle|^2 \quad \downarrow$$

$$\langle \phi_A | \Psi(t) \rangle = \sum_{nk} |\langle \phi_A | \psi_{nk} \rangle| e^{-iE_{nk}t}$$

So what... it looks the same! Let's examine the matrix element $\langle \phi_A | \psi_{nk} \rangle = \int_{N\,u.c.} dr\, \phi_A^*(r)\psi_{nk}(r)$ The integral is over the N unit cells for N kpoints (supercell) $\rightarrow$ "N u.c."

But $\phi_A(\vec{r}) \cong 0$ outside u.c. around origin so to high accuracy

$$\langle \phi_A | \psi_{nk} \rangle \cong \int_{home} \phi_A(r)^* \psi_{nk}(r) dr \leftarrow \text{integral only over one unit cell about origin ("home" cell)}$$

Now over the supercell, $\psi_{nk}(r) = \frac{e^{ik\cdot r} u_{nk}(r)}{\sqrt{N}}$ is normalized to one.

$$\langle \phi_A | \psi_{nk} \rangle \cong \frac{1}{\sqrt{N}} \int dr\, \phi_A^*(r) e^{ik\cdot r} u_{nk}(r)$$

Now when we actually solve for Bloch solutions in a unit cell, we just find $u_{nk}(r)$ which is normalized to one over one unit cell (e.g. home) so $e^{ik\cdot r} u_{nk}(r)$ is the solution we normally find normalized for one unit cell.

For examples in tight-binding, we have

$$\psi_{nk}(r) = \frac{1}{\sqrt{N}} \sum_R e^{ik\cdot R} \chi_j(r-R) C_{jnk}$$

where R = lattice vectors

$\chi_j(r)$ = atomic basis orbitals in home cell $j = 1, \dots, n_{orb}$

and C_{jnk} comes from solving

$$\sum_{j'} \mathcal{H}^k_{jj'} C_{j'nk} = E_{nk} \sum_{j'} S^k_{jj'} C_{j'nk}$$

$$\mathcal{H}^k_{jj'} = \sum_R e^{ik\cdot R} \mathcal{H}_{jj'}(R)$$

$$S^k_{jj'} = \sum_R e^{ik\cdot R} S_{jj'}(R)$$

and $\mathcal{H}_{jj'}(R) = \langle \chi_j(r) | \mathcal{H} | \chi_{j'}(r-R) \rangle$

$S_{jj'}(R) = \langle \chi_j(r) | \chi_{j'}(r-R) \rangle$

All of this is as usual.

Now, when computing $\langle \phi_A | \psi_{nk} \rangle$ we only care about $\psi_{nk}(r)$ close to $\vec{r} = 0$ in home cell. So only $R = 0$ contributes:

$$\phi^*_A(r) \psi_{nk}(r) \equiv \frac{1}{\sqrt{N}} \phi^*_A(r) \sum_j \chi_j(r) C_{jnk}$$

This is just $1/\sqrt{N}$ time $\phi^*_A(r)$ time "usual" Bloch solution

So the only difference from infinite case is introduction of k & $1/\sqrt{N}$ which is to be squared.

Final procedure:

$$P_A(t) = |\langle \phi_A | \Psi(t) \rangle|^2 \quad \&$$

$$\langle \phi_A | \Psi(t) \rangle = \frac{1}{N} \sum_{nk} |\langle \phi_A | \tilde{\psi}_{nk} \rangle|^2 e^{-iE_{nk}t}$$

where $\tilde{\psi}_{nk}(r) = e^{ik\cdot r} u_{nk}(r)$ is normalized to 1 over one unit cell

So we sample over k points & average them.

With symmetry, sum over irreducible k set & use weight W_k instead of $\frac{1}{N}$.

$$\sum_{k_{irr}} W_{k_{irr}} = 1 \text{ is needed.}$$